UNIVERSITI PUTRA MALAYSIA

ADSORPTION OF COPPER (II) IONS IN AQUEOUS SAMPLES USING EFFERVESCENCE-AMINO-ZEOLITE

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By

JAMJOUM HAYFA ALAJILANI ABRAHEEM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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November 2020

Chair : Sazlinda Binti Kamaruzaman, PhD
Faculty : Science

Heavy metals, the non-degradable elements of the earth's crust, have many adverse effects on the human body. Their presence in the water environment poses serious health risks to other living organisms as well. Industrial wastewater also contains large amounts of copper ions, which migrate through soil and aquatic streams into the atmosphere and ultimately accumulate along the food chain, causing human beings to face health risks. Excessive human intake of copper ions contributes to severe mucosal irritation and corrosion, hepatic and renal damage, widespread capillary damage, severe gastrointestinal irritation, central nervous system irritation, and potential liver and kidney necrotic changes. Therefore, Cu^{2+}ions are considered for removal. Several products have been used to control sorption contaminants, including granulated activated carbon, zeolite, montmorillonite, peat, and compost. The main objective of the current study was to synthesize and characterize EFF-APTES-zeolite using different techniques. The removal of Cu^{2+} ions was investigated using synthetic solutions at different ion concentrations, contact time, EFF-APTES-zeolite dosage, temperature, and sample pH. The findings of the current study have shown that EFF-APTES-zeolite has been successfully synthesized and characterized by FT-IR, FE-SEM and BET methods. The results of the current study also showed that the optimal dose for Cu^{2+} removal was 20 mg with 99.21%, while the optimum concentration was 100 ppm with 99.20%. Similarly, the pH of 4 is the optimum value for EFF-APTES-zeolite to extract 99.99% of Cu^{2+} metal ions from aqueous water. In the meantime, the contact time of 15 min was the optimum period for the successful removal of Cu^{2+} from aqueous samples. Lastly, 30℃ was noted to be the best temperature for EFF-APTES-zeolite to efficiently remove Cu^{2+} ions (99.69%) from aqueous water. The adsorption kinetics analysis demonstrated a pseudo-first-order and pseudo-second-order adsorption model for Cu^{2+} ions using EFF-APTES-zeolite. This suggests that the adsorption can be regulated by chemical adsorption. Both the Langmuir and Freundlich models match the balance data well, suggesting the presence of a monolayer adsorption with a high adsorption potential for Cu^{2+} at different concentrations.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PEJERAPAN ION TEMBAGA DALAM SAMPEL AKUAS MENGGUNAKAN PEMBUAKAN AMINO ZEOLIT

Oleh

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Logam berat ialah unsur-unsur kerak bumi yang tidak dapat dimusnahkan, mempunyai banyak kesan buruk terhadap tubuh manusia. Kehadiran mereka di dalam air menimbulkan risiko kesihatan yang serius bagi organisma yang lain. Air buangan industri juga mengandungi sejumlah besar ion tembaga, yang berpindah melalui tanah dan aliran air ke atmosfera dan akhirnya memasuki rantai makanan, menyebabkan risiko kesihatan kepada manusia. Pengambilan ion tembaga yang berlebihan menyumbang kepada kerengsaan dan korosi mukosa yang teruk, kerosakan hati dan renal, kerosakan kapilari yang meluas, kerengsaan gastrousus yang teruk, kerengsaan sistem saraf pusat, dan potensi perubahan nekrotik hati dan ginjal. Oleh itu, ion Cu^{2+} dipertimbangkan untuk disingkirkan. Beberapa bahan telah digunakan untuk mengawal penyerapan bahan tercemar seperti karbon aktif berbutir, zeolit, montmorillonit, gambut dan kompos. Objektif utama kajian ini adalah untuk mensintesis dan mencirikan EFF-APTES-zeolite menggunakan teknik yang berbeza. Penyingkiran ion Cu^{2+} dikaji menggunakan larutan sintetik pada kepekatan ion yang berbeza, masa hubungan, dos EFF-APTES-zeolit, suhu, dan pH sampel. Hasil kajian semasa menunjukkan bahawa EFF-APTES-zeolite telah berjaya disintesis dan dicirikan melalui kaedah FT-IR, FE-SEM dan BET. Hasil kajian semasa juga menunjukkan bahawa dos optimum untuk penyingkiran Cu^{2+} adalah 20 mg dengan 99.21%, sementara kepekatan optimum adalah 100 ppm dengan 99.20%. pH 4 adalah nilai optimum untuk EFF-APTES-zeolite untuk mengekstrak 99,99% ion logam Cu2+ dari larutan akuas. Sementara itu, masa hubungan 15 min adalah tempoh paling optimum untuk berjaya menyingkirkan Cu^{2+} dari larutan akuas. Suhu 30 °C adalah suhu terbaik bagi EFF-APTES-zeolite untuk mengeluarkan ion Cu^{2+} (99.69%) dari air berair dengan cekap. Analisis penjerapan menunjukkan model penjerapan pseudo pertama dan pseudo kedua untuk ion Cu^{2+} menggunakan EFF-APTES-zeolite. Ini menunjukkan bahawa penjerapan berlaku dengan penjerapan interaksi kimia. Kedua-dua model Langmuir dan Freundlich sesuai dengan data keseimbangan, menunjukkan adanya penjerapan satu lapisan dengan potensi penjerapan yang tinggi untuk Cu^{2+} pada kepekatan yang berbeza.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

APTES	Aminopropyltriethoxysilane
EFF	Effervescence
BET	Brunner-Emmet-Teller
Cu^{2+}	Copper (II) Ion
FTIR	Fourier Transformed Infrared Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
WHO	World Health Organization
USEPA	The United States Environmental Protection Agency
$(SiO_4)^{4-}$	Orthosilicate Ion
$(AlO_4)^{5-}$	Aluminate
N_2O	Nitrous Oxide
TCEC	Total Cation Exchange Capacity
ECEC	Effective Cation Exchange Capacity
TGA	Thermal Gravimetric Analysis
AlPOs	Porous aluminophosphates
SAPOs	silicoaluminophosphates
HM	Heavy Metal
NaH_2PO_4	Monosodium phosphate
$NaHCO_3$	Sodium bicarbonate
ICP-OES	Inductively coupled plasma - optical emission spectrometry
Mg	Milligram
mL	Millilitre
L	Litter
mmol/g	Millimole per Gram

ppm	Parts per million
R^2	Correlation coefficients
t	Time
h	Hours
min	Minutes

CHAPTER 1

INTRODUCTION

1.1 Preamble

In the present work, $Cu^{2+,}$ as an example of heavy metal ions, investigated to remove collected aqueous samples using modified zeolite adsorption. Samples obtained, zeolites were modified using APTES to obtain micro-size powders and then using Effervescence converted into EFF-APTES-Zeolite. FT-IR (Fourier transformed infrared spectroscopy) was used to characterize the prepared biosorbent materials. Adsorption experiments were performed at various pH parameters, contact time, the biosorbent doses, and the initial concentration of Cu^{2+}. Furthermore, adsorption isotherms, Langmuir, Freundlich, and modeling kinetics were studied. According to the Langmuir model, adsorption capacities at their maximum were achieved at 250 and 125 mg/g for biosorbent materials, respectively. The adsorption process is based on the pseudo-second-order kinetic model.

1.2 Background Study

Water is a transparent, tasteless, odorless, and colorless chemical substance that is very important in our day-to-day life. Water is critical for all types of organisms, although it offers no calories or organic nutrients. Therefore, it is essential to improve and protect the quality of water. The point and non-point water contamination resources are continuously polluting our water resources (Bouwer, 2000; Chatterjee, 2007). The point source is a particular and distinguishable cause of water pollution, including a pipe or a drain, while the impacts that occur over a wide-ranging region, not accredited to a single source, are non-point sources of water pollution. The point source of water pollutions can be further categorized into organic, inorganic, and biological pollutants (Gupta & Deep, 2018). The most extensively documented inorganic pollutants of water are heavy metals, which are extremely detrimental and carcinogenic.

Additionally, sulfates, nitrates, phosphates, oxalates, fluorides, and chlorides possess severe effects on humans' health. Heavy metals are non-degradable compounds that can reach the human body through drinking water and food from the earth's crust. While some heavy metals, like copper (Cu^{2+}), lead (Pb^{2+}), and zinc (Zn^{2+}) are essential for human metabolism, however, they can be harmful to human health at a higher concentration (Chowdhury, Mazumder, Al-Attas, & Husain, 2016).

Generally, Cu^{2+} ions are linked with gastro-intestinal disorders, diarrhea, stomatitis, tremor, vomiting, paralysis, depression, and pneumonia (Singh, Vorst, Singh, & Lao, 2007). Cu^{2+} ion is a reddish-brown metal and necessary micronutrients for the development of animals and plants. It is also useful for the formation of blood haemoglobin. Although a moderate level of Cu^{2+} is beneficial for humans' health, its high concentration may lead to anaemia, liver, kidney, stomach, and intestinal diseases (Mahmoud, Nabil, & Mahmoud, 2015). Cu^{2+} ion has a strong affinity for the organic matter of the soil. At pH 5.5, the solubility of the Cu^{2+} ion accelerated, adjacent to the idyllic farmland range of 6-6.5. The adsorption process is recently considered as an economical, selective, and efficient approach for water treatment and analysis objectives worldwide due to the need for environmentally friendly and more viable technologies WHO, 2008. Because of low metal removal capacities and high-cost coal-based activated carbon, several advantages have been proved excellently to use the adsorption process with other agricultural materials, including its low-cost, accessibility, effectiveness, ease of operation competence to other conventional methods (Trivunac & Stevanovic, 2006). In waste water, heavy metals are not biodegradable and tend to pile up in living organisms and are toxic or carcinogenic to specific heavy metal ions. Heavy metal ion existence in water environment poses significant health threats to humans and other living species. Industrial wastewater also contains large quantities of copper ions, which migrate through soil and aquatic streams into the atmosphere and ultimately accumulate along with the food-chain, making human beings suffer from health hazards. Copper can be present in food as a contaminant.

While it functions together with specific proteins and enzymes in bones' formation, at higher concentrations, it induces critical toxic effects. Excessive human copper ion ingestion leads to extreme discomfort and degradation of the mucosa, hepatic and renal loss, extensive capillary damage, severe gastrointestinal irritation, irritation of the central nervous system, and possible necrotic changes in the liver and kidney. This severe health issue is the reason for selecting Cu^{2+} ions among all heavy metals for removal (Arbabi & Golshani, 2016). However, the World Health Organization has suggested a maximum of 2 mg/L as the provisional guideline value for drinking water's copper content. Excessive Cu^{2+} ions impair the osmoregulatory function of freshwater animals in freshwater resources and aquatic habitats. The United States Environmental Protection Agency (USEPA) has set acceptable limits of 1.3 mg/L in industrial effluents for copper ions (Arbabi & Golshani, 2016).

Natural zeolites have been used to enhance new adsorbents because of their chemical modification to increase their binding capacity (Sayari & Hamoudi, 2001). However, the natural zeolites have been modified to increase the adsorption efficiency in recent years by controlling their pore sizes and introduce a wide variety of functional groups onto the surface. The parameters, adsorption equilibrium, and thermodynamic for the adsorption method are studied. The Freundlich and Redlich Peterson models have described the study's equilibrium adsorption data (Y. Zhang, Yu, Cheng, Wang, & Ma, 2017). The pseudo-second-order model indicated that the adsorption method is chemisorption. These products can also eliminate the ammoniacal nitrogen from industrial waste water that occurs with other carbon-based compounds. Zeolites are hydrated aluminosilicate minerals containing negative charges on their surface, balanced by exchangeable cations (Ca^{2+} and Na^{2+}), and exchanged by other cations (Zn^{2+} and Cd^{2+}) (Doula, 2006; Inglezakis, Loizidou, & Grigoropoulou, 2002). In industries, zeolites can be used as sorbents, soil amenders, ion exchangers, and molecular sieves (Ayaz & DeVol, 2003). Zeolites contain a bulky surface area with great desirability for metal ions, due to which they are capable of providing a practical adventuring pathway for heavy metals in toxic systems (Pan, Zhang, Chen, Zou, & Yan, 2006). Zeolites consist of two types, natural zeolites, and synthetic zeolites. Zeolites are hydrated aluminosilicate porous minerals with significant physicochemical characteristics like cations exchanges, molecular sieving, catalysis, and sorption.

Due to their low-cost, efficient mechanical and thermal characteristics, zeolites are useful in water and wastewater treatments (Ji et al., 2012; Misaelides, 2011). Based on their high cations exchanges, polarity, and hydrophilicity, the use of zeolites has been focused on NH^{4+} (Franus & Wdowin, 2010), heavy metal ions (Korkuna et al., 2006), 2006), and polar organic pollution such as synthesized thiol- and amino-functionalized SBA-15 materials (Cai et al., 2006; Del Rio, 2015). On the other hand, various research has been conducted in laboratories to improve the production of zeolites. It has mainly been reported that the application of modified zeolite to remove pollutants and enhance the adsorption ability under physical, chemical, and composite modifications due to pores of the natural zeolite can activate blocking problems because of contaminants (Kragović et al., 2012).

Physical modifications such as thermal and ultrasonic modifications can increase the adsorption efficiency by reducing the surface resistance and remove impurities in the zeolite pores (Cherny et al., 2015). Chemical modifications such as acid-base, salt, a cationic surfactant, and rare earth modifications have been used to improve the adsorption ability (Sancho et al., 2017). Besides, composite modifications combine several modifying methods, including ultrasonic, heating, and alkali/acid/salt composite modifications. Enhanced zeolite does have best ammonium adsorption effect, 0.8 mol/L is the concentration of NaCl with ultrasonic power of 560W, the 40 minutes of time with a significant 91.1 percent removal rate; the equilibrium time is only 10 min compared to 60 minutes of natural zeolite (J. Wang, Liu, Liu, & Park, 2017).

1.3 Problem Statement

Heavy metals are poisonous, neurotoxic, mutagenic, and carcinogenic compounds predominantly present in contaminated environment water samples. Contamination of heavy metals can influence the growth of organisms and conceivably modify the features of our human culture that, in turn, influence the ability of the future to live on (Alluri et al., 2007). Additionally, in environmental water samples, the unjustified removal of heavy metal ions triggers ecological concerns globally due to their negative impact on human health (J. Wang et al., 2017). Many techniques have been employed to remove heavy metal ions, especially Cu^{2+}, such as reverse osmosis, chemical precipitation, ion exchange, ultrafiltration, and adsorption (Gunatilake, 2015).

Among all the processes mentioned above, the adsorption method is preferable because it is economically advantageous, highly efficient, and applicable. Two essential factors need to be considered during the adsorption process: the overall process's set-up and the adsorbent's selection. The stirring method by utilizing a magnetic stirrer is the most widely used technique in the adsorption process, as this method will increase the contact time between the adsorbent and analyte (WHO, 2008). Activated carbon is considered the best adsorbent employed in removing Cu^{2+} ions due to its substantial surface area and optimal adsorption ability. However, the rapid dispersion rate of the activated carbon during the adsorption process, leads to the particle's agglomeration towards the magnetic bar and challenging to be separated. The overall adsorption process becomes time-consuming and very impossible to conduct in-situ applications in the future.

Other than that, the cost of the activated carbon is expensive and usually requires a high amount of dosage (>100 mg) to achieve high efficiency of removal of more than 90% (Trivunac & Stevanovic, 2006). In recent years, the adsorption of heavy metal ions using zeolite is introduced due to the low-cost, and most of the metal ion is easily removed from the absorbent. Nevertheless, due to the zeolite surface's nature hydrophilicity, the adsorption efficiency became limited towards the cationic analyte.

Modification on zeolite's surface is needed to increase the selectivity and adsorption capacity towards Cu^{2+} ions to solve this problem (Hamoudi, Belkacemi, Sayari, & Larachi, 2001). According to the reported study on the limitation of the current adsorption method, the alternative adsorbent with a more effective adsorption technique is required to solve time-consuming, costly method/material, limited selectivity, and low adsorption capacity in order to remove heavy metal ions in aqueous samples. In this study, aminated zeolite with the effervescent, known as (EFF-APTES-zeolite) is synthesized, prepared, and characterized. This synthesized adsorbent is utilized to adsorption of Cu^{2+} ion in lake water samples (Sancho et al., 2017). Therefore, current techniques such as mentioned above have limitations in rapid carbon dispersion, leading to the natural zeolite's agglomeration and maximum absorption potential.

The natural zeolite was modified with effervescent (which is bubbly or fizzy) 3-aminopropyltrimethoxysilane (APTES) $[NH_2(H_2)Si(OC_2H_5)_3$ in this technique to create amino zeolite that improves the absorptive properties of existing zeolite due to their phobic contamination towards the anionic ions and hydro. In comparison with the unmodified natural one, these synthesized zeolites show high absorption capacity due to their peculiar amino functional group and hydrophobicity property (Gao et al., 2018).

1.4 Significance of the Study

The adsorption method is one of the preferable technologies to remove heavy metals because it is economically, highly efficient, and easily applicable. Two essential factors need to be considered during the adsorption process: the overall process's set-up and the adsorbent's selection. The stirring method by utilizing a magnetic stirrer is the most widely used technique in the adsorption process, as this method will increase the contact time between the adsorbent and analyte. The 3-aminopropyl triethoxysilane (APTES) was employed to remove Cu^{2+} from the aqueous solutions in the current research. The aptitude of the amino-zeolite ions exchanges to eradicate the Cu^{2+} ions employing the ion-exchange technique has been reported by (Shaaran, 2009). The adsorption performance of the effervescence APTES is one of the most common binding reagents for heavy metals removal, as it could provide amine groups to remove Cu^{2+} through interaction amine groups with negatively charged. Therefore, the adsorption process's performance using EFF-APTES-zeolite was discussed in terms of impacts of the adsorbent dosage, metal ion concentration, pH, and the temperature. The probability of frequent utilization of Cu^{2+} ions has been examined through desorption-adsorption tests. This study provides a direction for future utilization of organic EFF-APTES-zeolite as an effective method in removing Cu^{2+} ions from contaminated environment water samples.

1.5 Research Objectives

The current study has the following objectives;

1. To synthesize and characterize the effervescent APTES-zeolite.
2. To optimize several adsorption parameters for removing Cu^{2+} ions in aqueous samples, such as adsorbent dosage, sample pH, contact time, initial concentration, and adsorption temperature.
3. To study the performance of effervescent APTES-zeolite with the removal of Cu^{2+} ions in aqueous samples from lake and determine the adsorption study by using kinetic and isotherms study.

1.6 Thesis Organization

The thesis has been divided into five chapters. This section deals with the brief description of each chapter.

Chapter 1
Present the concept of zeolite-based adsorption of Cu^{2+} ions from aqueous samples, background study, and the applications currently used. The problems associated with the present content, current research emphasis, objectives, and analysis scope is further addressed.

Chapter 2
Provides detailed literature and critical review of the physical properties of copper (Cu^{2+}) ions, details about the adsorption method, zeolites, their classification and functionalization, effervescence technique, and adsorption kinetics, which are extensively used in this research

Chapter 3
The third chapter gathers the information about the research materials used in synthesizing zeolites using the adsorption method for removal, characterization, and methodology in the fabrication and testing. Material specifications, synthesis procedure, FT-IR and other characterization techniques, adsorption kinetics, and isotherms are discussed.

Chapter 4
The fourth chapter is providing information about results, observations, and discussions from the study outcome. The effect of different parameters towards Cu^{2+} Ions Removal like temperature, ion concentration is studied in detail and the results from Adsorption kinetics and isotherm study.

Chapter 5
The fifth and last chapter giving the primary outcome of this research, work with overall conclusions and future aspects.

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PUBLICATION

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